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**COLLABORATIVE RESEARCH AND DEVELOPMENT
(CR&D)**

Delivery Order 0056: Novel Nanotube Synthesis

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Final Report

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14. ABSTRACT <p>This research in support of the Air Force Research Laboratory Materials and Manufacturing Directorate was conducted at the University of Pennsylvania in Philadelphia, PA from 31 July 2006 through 1 February 2008. This task worked to develop synthesis routes for nanotubes that are not pure carbon, e.g., boron nitride, boron-carbon nitride. Carbon nanotubes can be synthesized with relative ease in laboratory and commercial settings via simple catalytic chemical vapor deposition (CCVD) techniques; therefore, widespread access has allowed for intense study and application. BN nanotubes have proven more difficult to synthesize reliably or on scales that permit complimentary investigation and, consequently, less is known about these materials. BNNTs have been synthesized in a similar manner to carbon nanotubes such as arc discharge, laser ablation, ball milling, substitution reaction from carbon nanotubes, and chemical vapor deposition, but standard CCVD methods which enable high quality and large scale synthesis of CNT have not been properly adopted for the BNNT synthesis. Herein, we developed catalytic methods and report the achievement on the growth of BN nanotubes via catalytic pyrolysis and CVD route.</p>						
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1.0 INTRODUCTION

Carbon nanotubes (CNTs) have been the focus of nanoscale research due to remarkable electronic, mechanical and optical properties, but their applications are limited by the fact that semiconducting nanotubes are mixed with metallic nanotubes in as-grown samples. Boron nitride nanotubes (BNNTs) are structural analog of carbon nanotubes such that alternating boron and nitrogen atoms replace carbon atoms in a hexagonal lattice structure. This elemental change gives significant advantages over carbon nanotubes such as uniform band gap (~ 5 eV) insensitive to their diameters and chiralities, band gap tunability by the giant stark effect, and high temperature oxidation resistance up to 800 °C. These properties make BNNTs attractive for nanoscale application such as nanoelectronics, optoelectronics, and nanocomposite. Carbon nanotubes can be synthesized with relative ease in laboratory and commercial settings via simple catalytic chemical vapor deposition (CCVD) techniques; therefore, widespread access has allowed for intense study and application. BN nanotubes have proven more difficult to synthesize reliably or on scales that permit complimentary investigation and, consequently, less is known about these materials. BNNTs have been synthesized in a similar manner to carbon nanotubes such as arc discharge, laser ablation, ball milling, substitution reaction from carbon nanotubes, and chemical vapor deposition, but standard CCVD methods which enable high quality and large scale synthesis of CNT have not been properly adopted for the BNNT synthesis. Herein, we developed catalytic methods and report the achievement on the growth of BN nanotubes via catalytic pyrolysis and CVD route.

2.0 ACHIEVEMENT

2.1 Catalytic pyrolysis for BN nanotube synthesis

Pyrolysis of polyborazylene with assistance of transition metal nanoparticle catalyst at 1100-1200 °C was initiated by Pender et al. This method has been pursued for a while, but we found that this method produced short multi-walled nanotubes, bamboo like structures, and stack of caps structures (Figure 1). As illustrated in Figure 1b, iron oxide nanoparticle appears to be a right catalyst showing shape matching between edge of a nanotube and a nanoparticle. Prevention of catalyst aggregation is critical to produce perfect shaped BN nanotubes, but it has not been completely achieved yet.

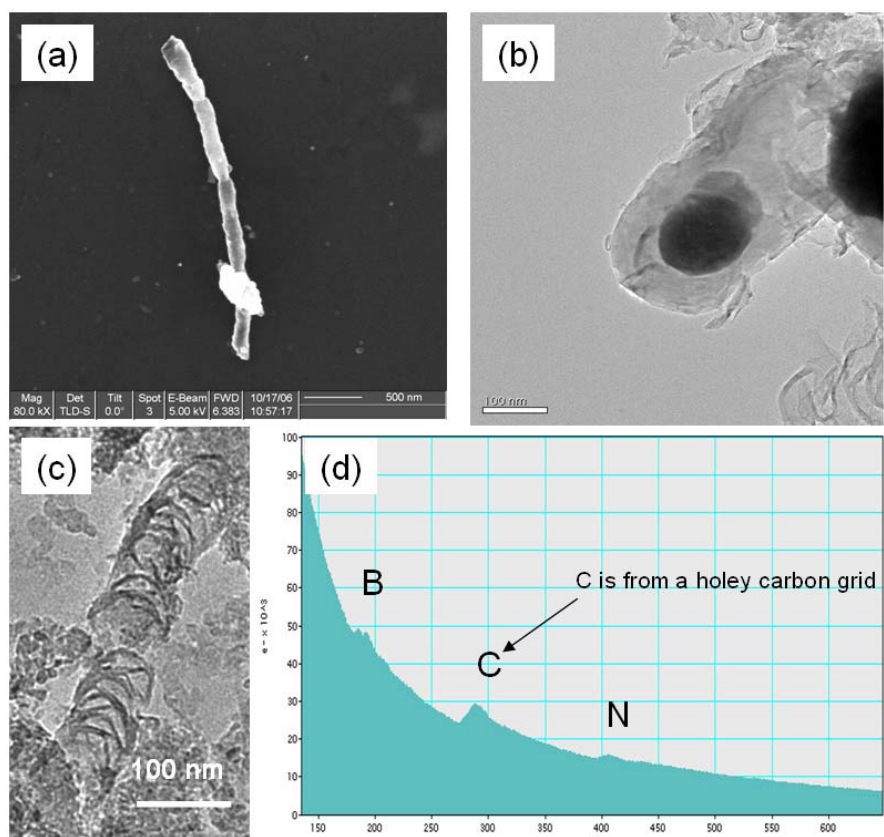


Figure 1. (a) SEM and (b), (c) TEM images (d) EELS data from the BN nanotubes produced by pyrolysis of polyborazylene. (Kim et al. – unpublished results).

2.2 Precursor synthesis

One of the limiting factors in BN nanotube synthesis is a lack of suitable precursor for catalytic CVD. In this regard, borazine, a BN analog of benzene could be a perfect binary precursor for BN nanotube synthesis. Borazine was synthesized according to the previous report from Sneddon et al. An intimate mixture of 30.7 g (0.81 moles) of NaBH_4 (Aldrich) and 82.3g

(0.62 moles) of NH_4SO_4 (Aldrich) was prepared. The mixture was added, under a nitrogen flow to 350ml of tetraglyme in a 2L three-neck round bottomed flask fitted with a thermometer and a reflux condenser. The exit of the condenser was connected to a standard vacuum line with a mechanical pump through four liquid nitrogen traps. Hydrogen evolution begins immediately and is released through an oil bubbler. Once the foaming subsides, the mixture is heated to 70 °C over 1 hour. After that, the oil bubbler is closed and the borazine is pulled through four liquid nitrogen traps, for the next three hours, while gradually raising the temperature to 135 °C. The borazine thus collected in the liquid nitrogen traps was further purified by a single vacuum fractionation using traps at -45 °C, -78 °C and -196 °C. In the -78 °C trap 13.1g (0.16 moles, 60% yield based on starting BH_4^-) was condensed. Since borazine is air sensitive, the purified borazine was stored in a freezer. Other precursors such as vinyl borazine and 1-hexylborazine for BCN and BC_2N nanotubes are being developed and attempted to be used for CCVD in Professor Sneddon's group at Penn.

2.3 Catalytic CVD for BN nanotube synthesis

Synthesis of multi-walled and double-walled BN nanotubes has been achieved via catalytic chemical vapor deposition from the precursors. Multi-walled BN nanotubes were synthesized from boron powder mixed with MgO and FeO over 1300 °C in a manner similar to Bando's report but produced here in a general setup using a quartz tube furnace (Figure 2). As illustrated in Figure 2, the grown tubes are high quality and pure multi-walled BN nanotubes.

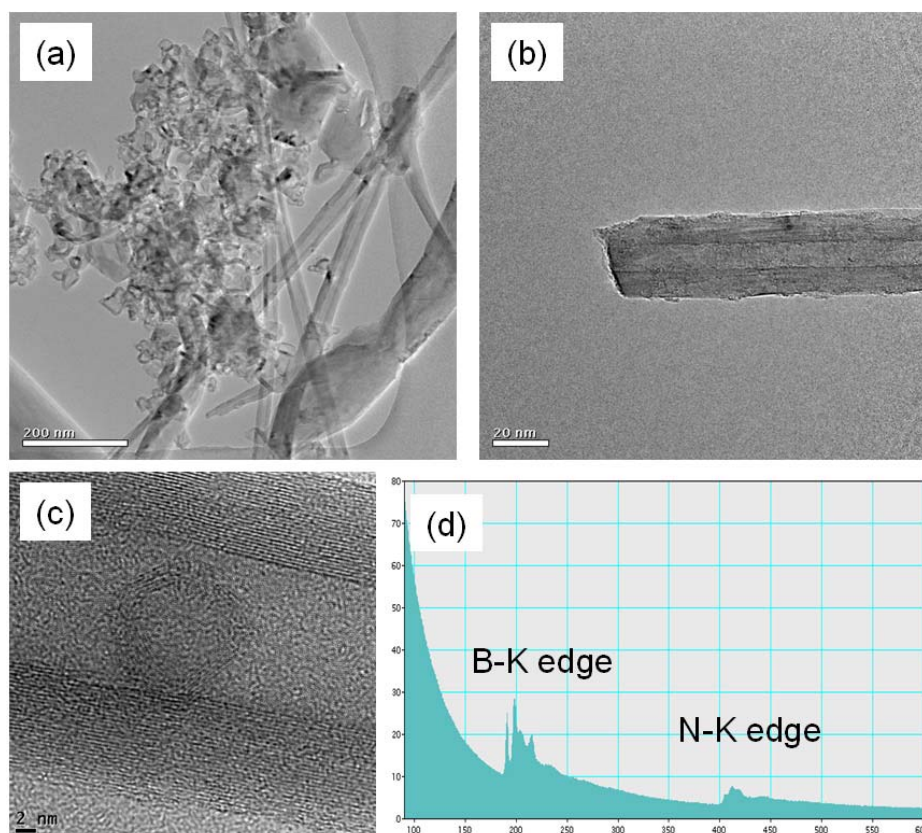


Figure 2. (a), (b) Low and (c) high resolution TEM images and (d) EELS data shows that multi-walled nanotubes were grown from a mixture of B, MgO, and FeO. (Kim et al.-unpublished results).

Double-walled BN nanotubes were synthesized by CCVD method using a floating catalyst (nickelocene) for the first time (Figure 3). Proper purification and handling of borazine enabled adjustment of the vapor pressure of borazine by changing temperature such that double-walled BN nanotubes were dominantly formed at lower vapor pressure of borazine over 1000 °C. At higher vapor pressure of borazine, BN nanofibers were produced rather than nanotubes. Floating catalyst method with nickelocene is expected to produce BN nanotube materials continuously in a similar manner to HipCo or CoMoCat process for carbon nanotube synthesis.

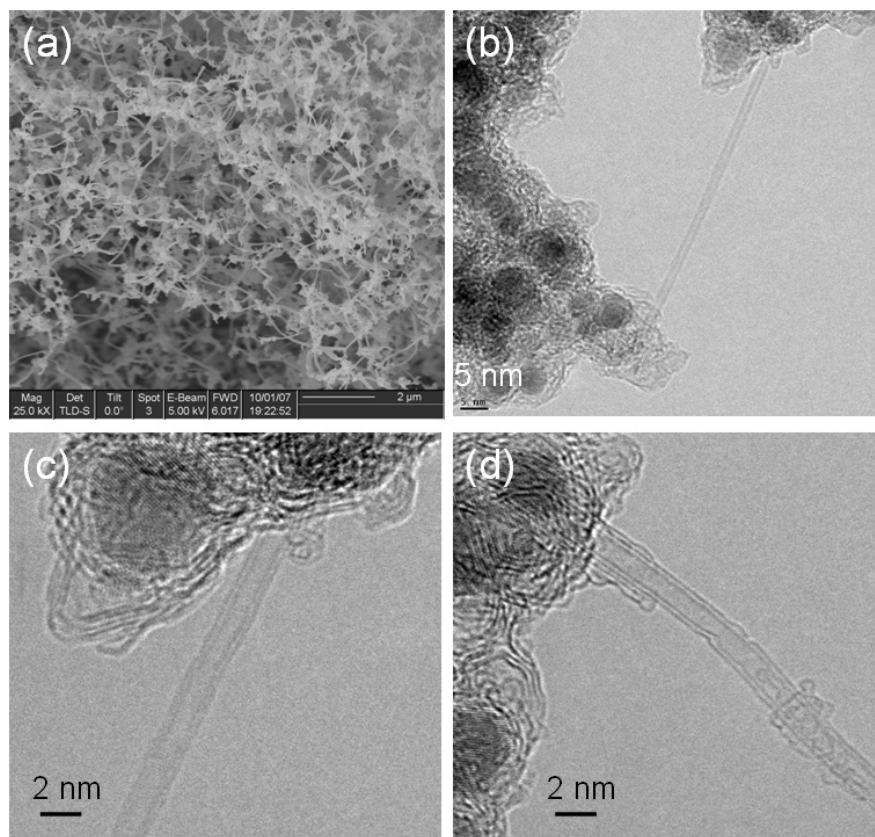


Figure 3. (a) SEM, (b) low and (c), (d) high resolution TEM images show double-walled BN nanotubes were grown by catalytic CVD method. (Kim et al.-unpublished results).

3.0 CONCLUSION

1. Pyrolysis route and catalytic chemical vapor deposition (CCVD) route for BN nanotube synthesis have been pursued.
2. Pyrolysis of polyborazylene mixed with nanoparticles produced bamboo, stack of cap, and multi-wall BN nanotube structures.
3. CVD growth of multi-walled BN nanotubes has been achieved from boron power in a manner similar to Bando's group, but they were produced in a general setup using a quartz tube furnace, and this method has scale up possibility.
4. Catalytic CVD method for the BN nanotube synthesis using floating catalyst, nickelocene was developed for the first time. At lower vapor pressure of borazine, double-walled BN nanotubes were produced while BN nanofibers were produced at higher vapor pressure.
5. TEM, SEM, and EELS was performed to characterize BN nanotube structures and chemical composition.